Sept. 11, 1956 M. D. BARNES 2,762,698

FERTILIZER MANUFACTURE AND URANIUM RECOVERY

Filed March 22, 1952

3 Sheets-Sheet 1

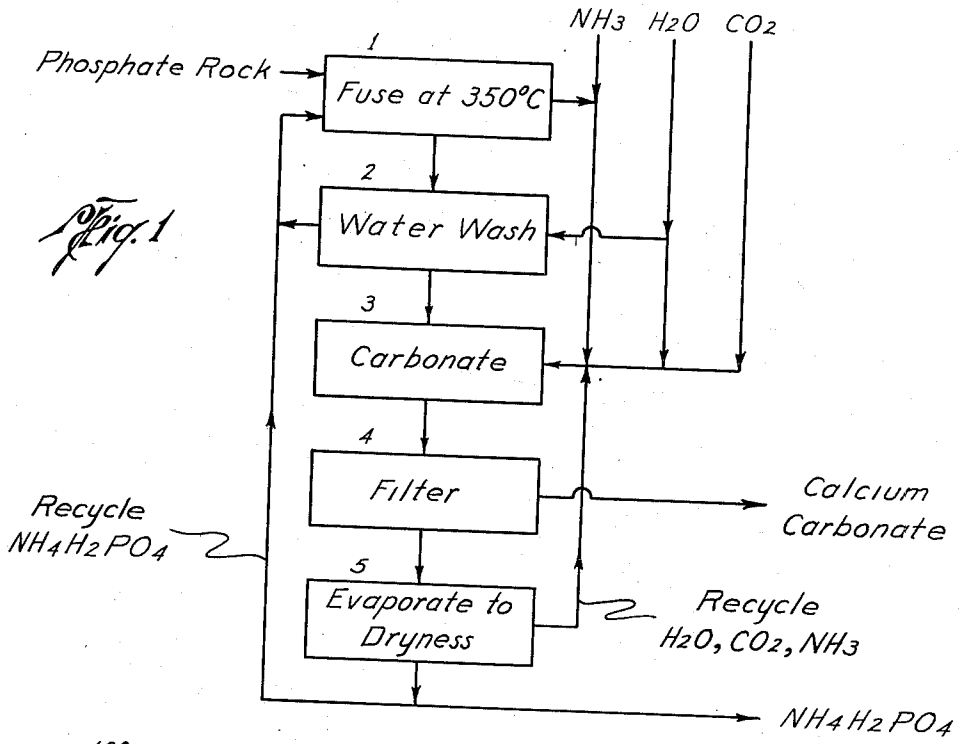


Fig. 1

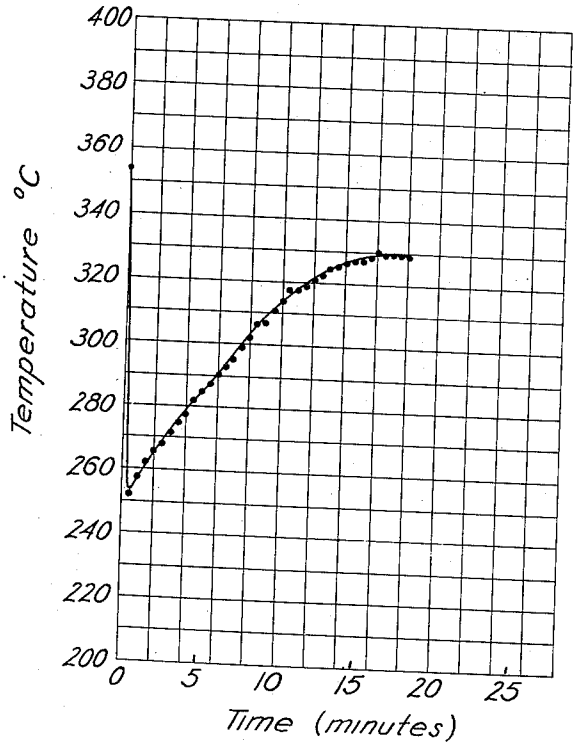


Fig. 2

furnace temp. 350°C
P_2O_5 yield 74.1%

Marion D. Barnes
INVENTOR.

BY Lewis H. Wilson

ATTORNEY

Sept. 11, 1956 M. D. BARNES 2,762,698

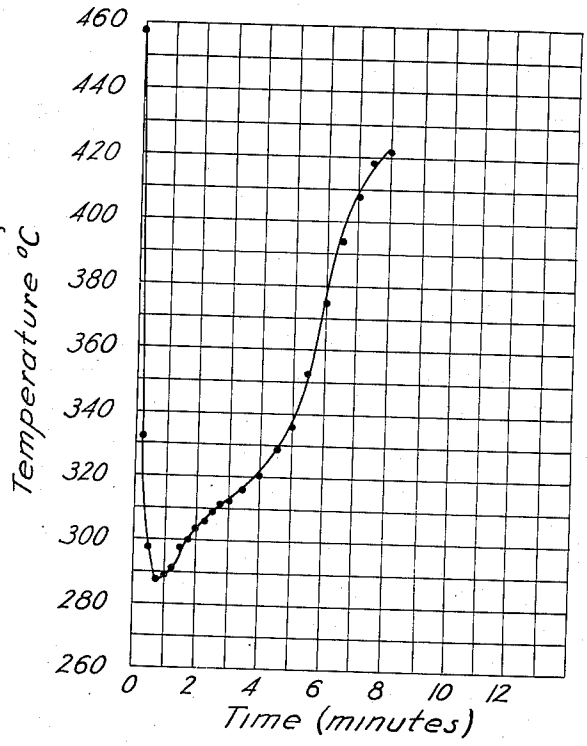
FERTILIZER MANUFACTURE AND URANIUM RECOVERY

Filed March 22, 1952

3 Sheets-Sheet 2

Fig. 3

furnace temp. 450°C
P_2O_5 yield 88.2%



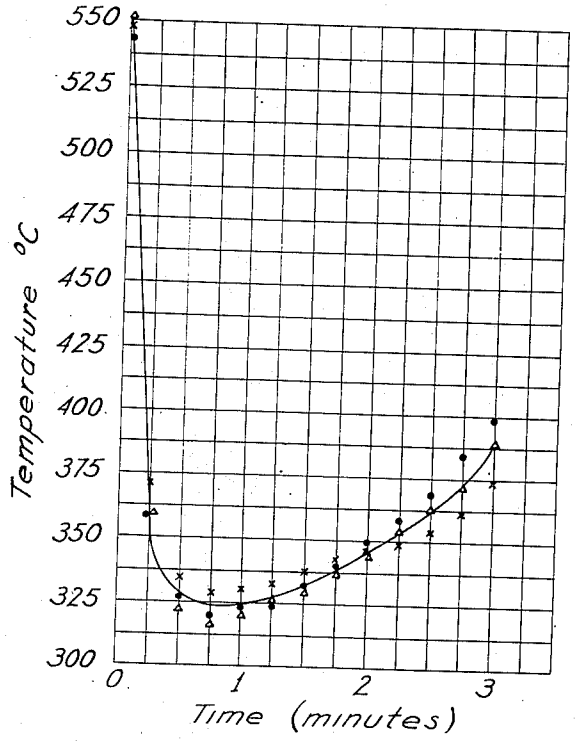


Fig. 4

furnace temp. 550°C
P_2O_5 yield 90.2%

Marion D. Barnes
INVENTOR.

BY Lewis H. Wilson

ATTORNEY

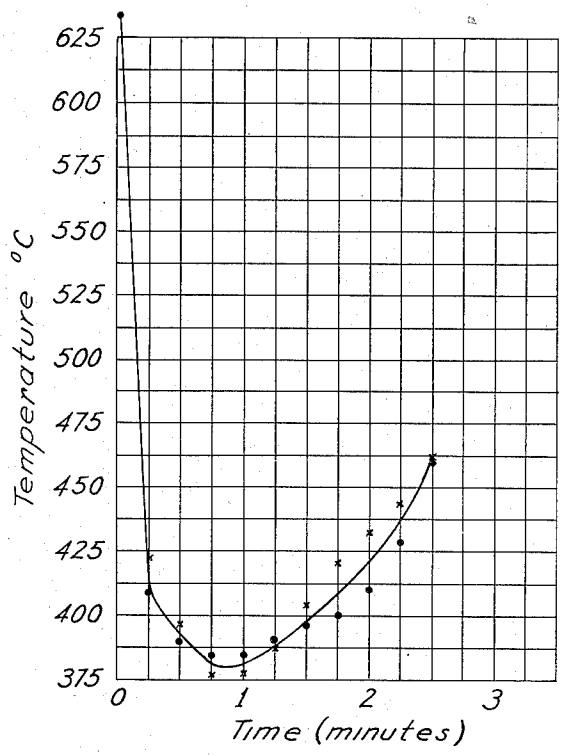
Sept. 11, 1956 M. D. BARNES 2,762,698

FERTILIZER MANUFACTURE AND URANIUM RECOVERY

Filed March 22, 1952 3 Sheets-Sheet 3

Fig. 5

furnace temp. 650°C
P_2O_5 yield 89.2%



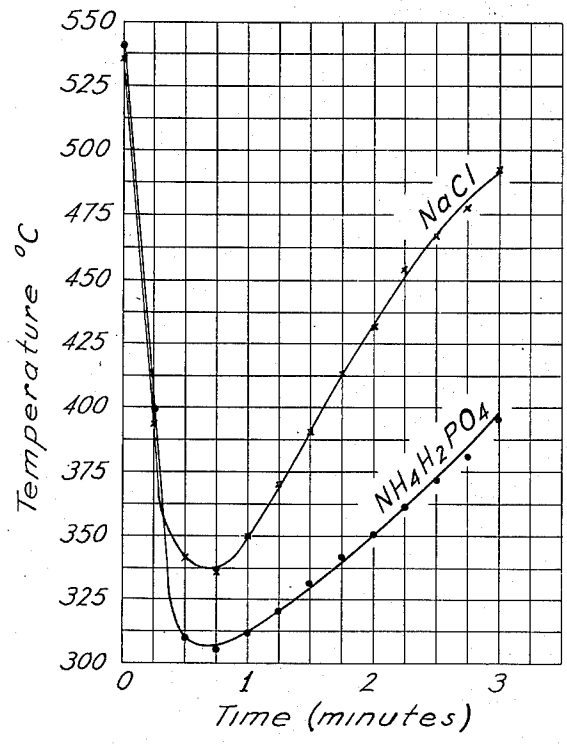


Fig. 6

furnace temp. 550 °C

Marion D. Barnes
INVENTOR.

BY Lewis H. Wilson

ATTORNEY

United States Patent Office 2,762,698 Patented Sept. 11, 1956

2,762,698

FERTILIZER MANUFACTURE AND URANIUM RECOVERY

Marion D. Barnes, El Dorado, Ark., assignor, by mesne assignments, to Monsanto Chemical Company, St. Louis, Mo., a corporation of Delaware

Application March 22, 1952, Serial No. 277,996
16 Claims. (Cl. 71—42)

This invention relates to the production of fertilizers and more particularly to a process of producing soluble phosphatic materials.

By the expression "soluble phosphatic materials" as used herein is meant water soluble as well as citrate soluble phosphatic materials. Dicalcium phosphate and calcium metaphosphate fall in the category of citrate soluble phosphatic materials. The term "metaphosphate" or "metaphosphates" involved in this invention cannot be construed to mean a specific composition or molecular species since neither the individual species nor structure of these materials are known. It is not known whether the "metaphosphate" is a monomer, copolymer or interpolymer or combination thereof, or to what extent it may be polymerized. This is true whether one has reference to the metaphosphates, the metaphosphoric acids, or even to P_2O_5. Even tricalcium phosphate exists in at least two different forms, e. g. the alpha and beta forms. It is well recognized in the literature that the properties of "metaphosphate" vary widely depending upon the process of making same. For instance, see Ephraim, Fritz, "Inorganic Chemistry," 4th ed., 1943, Interscience Publishers. At pages 727 and 729 of Ephraim the following two statements are made. "The relations of the metaphosphates are still so confused, in spite of numerous investigations, that the practice of giving definite formulae for the products must be given up for the present. . . ." ". . . free metaphosphoric acid can have very varied properties. Indeed, it can be syrupy and hygroscopic, or glassy and very sparingly soluble according to the method of preparation." Another interesting article along these lines is Partridge, Everett P., Chem. & Eng. News, 27, 214–217 (1941). In view of the foregoing it is intended that the term "metaphosphate" used herein be interpreted as defined by the process of making it.

Both of the following two major accomplishments must be effected in most processes for the manufacture of available phosphate for fertilizers. First, in all such processes it is necessary to decompose the apatite structure of the calcium-phosphorous containing material such as phosphate rock and thus render the P_2O_5 content of the rock available to plants as a food. Secondly, in most such processes it is necessary to separate the calcium oxide from the resulting mixture to such extent that the ratio of about 3.5 to 1 of calcium oxide to P_2O_5 in the initial phosphate rock will be reduced to a value in the resulting phosphatic material sufficiently low to minimize the reversion of the phosphatic mixture to tricalcium phosphate due to changing environment and conditions of said mixture, tricalcium phosphate being relatively unavailable to plants. In conventional fertilizer manufacture acidulation of phosphate rock with sulfuric acid almost without exception has been the means for obtaining the two above objectives. While in the conventional process of making regular superphosphate the calcium oxide is not separated from the P_2O_5, it is effectively tied up as calcium sulfate so that substantially no reversion takes place.

However, because of the increasing demand for higher analysis fertilizers and because of the increasing shortage and cost of sulfuric acid, the sulfuric acid process (the so-called wet process) for making fertilizers (regular and treble super phosphates) has serious drawbacks. Therefore, there is a pressing need for a process which avoids these drawbacks, i. e. a process for economically producing high analysis fertilizers without the use of sulfuric acid.

An object of this invention is to provide an improved process for making fertilizers. A further object is to provide a process for making high analysis fertilizers without the use of sulfuric acid or sulfur in any form. A still further object is to provide a process for making soluble phosphatic materials. The above and other objects will be apparent from the description of this invention given hereinafter.

This invention may be carried out in such manner as to produce from calcium-phosphorus containing materials, monoammonium phosphate, diammonium phosphate, ammonium metaphosphate or any combination thereof. Calcium-phosphorus containing materials applicable include any such materials which can be processed according to this invention to give the fertilizer products desired. However, because of its high P_2O_5 content, phosphate rock is the preferred calcium-phosphorus containing material.

The above and other objects can be accomplished according to this invention broadly by carrying out the process for producing soluble phosphatic materials which comprises fusing calcium-phosphorus containing materials and a portion of the product phosphatic materials, removing orthophosphatic material from the resulting melt, reacting the melt with ammonium carbonate, separating the calcium carbonate produced from the resulting phosphatic materials and recycling a portion of the latter to the fusion step.

The raw materials of the process are phosphate rock or other equivalent calcium-phosphorus containing material, ammonia, carbon dioxide, water and a portion of the phosphatic material produced which is recycled to the system for attacking the phosphate rock. The products are as stated above and the byproduct is calcium carbonate.

The accompanying drawings illustrate one embodiment of this invention and of the effect of certain variables.

Figure 1 illustrates in flow sheet form one embodiment of the invention.

Figures 2–5 show the effect of time and temperature of fusion.

Figure 6 shows something of the thermal nature of the fusion reaction.

Referring to the accompanying flow sheet (Figure 1), an embodiment of this invention will now be described in connection with preparing essentially monoammonium phosphate from phosphate rock. The process involves the two major phases of solubilizing the phosphate rock and transposing with ammonium carbonate the resulting calcium metaphosphate into monoammonium phosphate and calcium carbonate, a portion of the monoammonium phosphate being recycled and the calcium carbonate being filtered off. The process may conveniently be divided into five steps. In step 1 phosphate rock and monoammonium phosphate are fused to produce primarily calcium metaphosphate and some calcium othophosphate, the latter being separated out in step 2 and recycled to the fusion in order to avoid its reversion to insoluble tricalcium phosphate in step 3 wherein the calcium metaphosphate is transposed with aqueous ammonium carbonate to monoammonium phosphate and calcium carbonate, the calcium carbonate being filtered therefrom in step 4. In step 5 the filtrate is evaporated to produce the monoammonium phosphate product, a portion of

which is recycled to the fusion step. The ammonia, carbon dioxide and water evolved during step 5 are recycled to step 3.

The above embodiment of this invention involving the preparation of monoammonium phosphate from phosphate rock will now be described in greater detail with reference to the accompanying flow sheet (Figure 1). Step 1 involves the fusion of phosphate rock and the recycle portion of the monoammonium phosphate product. The fusion may be carried out by (1) first mixing the phosphate rock and monoammonium phosphate and then fusing the mixture, (2) or the monoammonium phosphate may be fused alone and mixed with phosphate rock and the resulting mixture fused, (3) or the monoammonium phosphate may be fused alone and a water solution of the fusion product used to digest the phosphate rock. While good results have been obtained by all of the above fusion methods, in general the best results have been obtained by (1) and the least satisfactory results have been obtained by (3). The fusion converts the tricalcium phosphate of the phosphate rock mostly to calcium metaphosphate and liberates ammonia and water from the monoammonium phosphate, the ammonia being returned to the system. Some orthophosphate remains in the fusion melt.

The monoammonium phosphate serves to attack the rock in such manner that the tricalcium phosphate thereof is decomposed and the calcium is tied up mostly as calcium metaphosphate. The ratio of monoammonium phosphate to phosphate rock required to do this satisfactorily varies directly with the amount of calcium oxide in the rock. Preferably a slight excess of monoammonium phosphate over that theoretically required will be used. For example, when using a typical phosphate rock, which has a calcium oxide content of about 45%, P_2O_5 yields upwards of 80% are obtained with a three to one ratio of monoammonium phosphate to phosphate rock. The above also applied if ammonium metaphosphate is substituted for the monoammonium phosphate, except that the ratio of ammonium metaphosphate to rock needed is only about 2.5/1.

Unless otherwise specified, P_2O_5 yields are given herein as per cent by weight of the P_2O_5 in the original phosphate rock.

Particle size of the rock has no substantial effect on the process, e. g. rock particle sizes varying between regular coarse commercial rock and minus 325 mesh are quite satisfactory.

Starting with four samples of phosphate rock, which were identical except for particle size, and subjecting each sample to the same conditions according to this invention, the yields of P_2O_5 shown in Table 1 below were obtained. The phosphate rock used in experiment 1 was regular commercial grind rock, 93.7% of which passed a 100 mesh screen. The samples of phosphate rock used in experiments 2, 3 and 4 were obtained by dividing commercial rock into three lots. From one lot, that portion which passed a 100 mesh screen was used in experiment 2; from another lot, that portion which passed a 200 mesh screen was used in experiment 3; and from the other lot, that portion which passed a 325 mesh screen was used in experiment 4.

TABLE 1

Phosphate rock particle size vs. P_2O_5 *yield*

Reference	Exp. No.	Particle Size	P_2O_5 Yield, Percent by Weight
79-182-1	1	commercial grind	89.28
79-182-2	2	−100 mesh	88.98
79-182-3	3	−200 mesh	83.43
79-182-4	4	−325 mesh	84.13

The temperature and time of fusion are much more significant than particle size. Time and temperature of fusion vary inversely. Yields of P_2O_5 in excess of 80% have been obtained by fusing at oven temperatures of 350° C.–650° C. for 20 minutes to 2.5 minutes, respectively. Yield of P_2O_5 is apt to be adversely affected by employing fusion conditions which are too drastic.

EXAMPLE 1

Figures 2–5 of the drawings and the following Example 1 illustrate the effect of fusion conditions on P_2O_5 yields. The conditions and results are summarized in table 2 below. For each oven temperature-fusion time combination shown, a number of experiments were carried out and the results are reported as an average. In each experiment the fusion mixture was prepared by mixing in a mortar 30 grams of monoammonium phosphate with 10 grams of phosphate rock, the phosphate rock having a P_2O_5 content of 34.4%. The particle size of the phosphate rock used was micronized (i. e. substantially all of it passes a 325 mesh screen) and the monoammonium phosphate was ground to pass a 20 mesh screen. A small rectangular fusion vessel was used. The fusion vessel contained a thermocouple well which passed through one side of the vessel at a point about midway between its two ends and terminated in the center of the vessel. The thermocouple well was parallel to the bottom of the fusion vessel and separated slightly therefrom. One end of a thermocouple lead was inserted in the thermocouple well so as to measure the temperature of the charge or melt separately from that of the oven by means of a potentiometer. The fusion vessel was placed in an automatic electric oven, the oven turned on and its temperature control set for the temperature desired. After the thermocouple temperature and oven temperature reached substantial equilibrium, the charge was placed in the vessel so that the thermocouple well was approximately in the center of the charge, the starting temperature of the oven being taken just prior to introducing the charge. The temperature of the melt was taken at intervals of 15 seconds throughout the prescribed fusion period.

The melt was removed and quenched by placing in an ice bath, and then ground. Ten grams of the fusion product was ground, washed with water, filtered, and the residue washed with water. The residue was slurried in a mixture of 15 grams ammonium bicarbonate, 7.5 ml. ammonium hydroxide and 25 ml. water and tumbled 4 hours in a citrate bottle. The calcium carbonate precipitate thus produced was filtered off and water washed. The P_2O_5 content of the carbonate filtrate, water wash and calcium carbonate cake was determined. Except for temperature of the melt, Table 2 below summarizes the data on experiments carried out as described above. The temperature of the melt is shown in Figures 2–5.

TABLE 2

Fusion time and temperature vs. P_2O_5 *yield*

Reference	Exp. No.	Furnace Temp., ° C.	Time, Mins.	P_2O_5 yield, Percent by Weight
95-135	1	350	20	74.1
95-134	2	450	8	88.2
95-123	3	550	3	91.9
95-118	4	650	2.5	89.2

It will be seen from Figures 2–5 that placing the cold charge on the hot thermocouple well resulted in a chilling effect causing a rapid temperature drop during the first few seconds of the fusion period, and then the temperature of the charge and that of the thermocouple well reached equilibrium and thereafter uniformly increased toward the furnace temperature. In order to get

mum temperature reached was 120° C.; and the pH dropped from approximately ten at the start to approximately five at the end of the evaporation. If a mixture of monoammonium phosphate and ammonium metaphosphate is desired, the filtrate is evaporated under conditions such that only a portion of the ammonium metaphosphate is hydrated to monoammonium phosphate.

The following will further illustrate the utility and versatility of this invention. (1) A portion of the calcium metaphosphate from step 2 can be taken off and used as such for fertilizer. There are many instances in which phosphate but no nitrogen is needed. Calcium metaphosphate serves this purpose well. In any event, however, a portion of the calcium metaphosphate must be processed for recycling. (2) A three-component mixed fertilizer can be made by dividing the carbonate filtrate (step 4) into two portions, adding a suitable source of potash (e. g. potassium chloride) to one portion and processing to product, and processing the other portion for recycle. Alternatively, a three-component fertilizer can be made by grinding potassium chloride or other suitable potash source with the product. (3) Alkali metal phosphates can be produced by reacting a portion of the calcium metaphosphate from step 2 with an aqueous solution of either sodium carbonate or potassium carbonate, and processing the remainder of the calcium metaphosphate to material for recycling to the fusion step.

In the event one should desire to separate out the monoammonium phosphate product by crystallization instead of by simple evaporation shown in the accompanying flow sheet (Figure 1), this can be done without crystallizing the recycle material. Accordingly, an alternative embodiment of this invention comprises fusing and water washing the fused melt as aforesaid, utilizing the water wash to convert to product by crystallizing monoammonium phosphate therefrom and centrifuging and drying same. This crystallization can be effected by evaporating a portion of the filtrate from step 4 under controlled conditions so as to minimize the evolution of ammonia and carbon dioxide. Then the calcium metaphosphate residue from the water wash is processed to obtain for recycling to the fusion step monoammonium phosphate by transposing said residue with ammonium carbonate, filtering out the resulting calcium carbonate precipitate and evaporating the filtrate. Thus, while the product material is made by crystallization under controlled conditions, the recycle material for the fusion step is made by simple evaporation according to the preferred embodiment of this invention described hereinbefore.

While phosphate rock is composed largely of tricalcium phosphate, it also contains appreciable amounts of impurities. The amounts and kinds of impurities vary with the type or grade of rock. These impurities affect any process for the manufacture of fertilizers from phosphate rock.

The amount and kind of impurities of a typical phosphate rock are shown in Table 3 below.

TABLE 3

Composition of Florida land pebble phosphate rock

	Percent
Moisture	1.34
Organic matter and combined water	0.85
Phosphoric acid [1]	32.30
Carbon dioxide [2]	2.78
Oxide of lime	46.14
Oxide of aluminum	1.08
Oxide of iron	1.14
Fluorine [3]	3.48
Sulfur trioxide	0.99
Titanium oxide	0.05
Manganous oxide	0.03
Insoluble siliceous matter	9.13
Magnesia	0.90
Alkalies as Na_2O	0.78
Undetermined constituents	0.47
	101.46
Less oxygen equivalents	1.46
	100.00

	Per cent
[1] Equal to B. P. L.	70.58
[2] Equal to $CaCO_3$	6.32
[3] Equal to CaF_2	7.15

The matter of impurities will now be discussed with respect to the present invention. Some of these impurities are insoluble in acid and others can be dissolved or reacted with strong acid. The siliceous matter and titanium oxide do not react with the fused monoammonium phosphate or fusion mixture. They leave the process with the calcium carbonate. Other materials also leave the process with the calcium carbonate after being attacked by the fusion mixture and subsequently converted with ammonium carbonate. Gaseous constituents are expelled during the fusion step, and can be removed from the process or returned to the carbonation step as desired.

The calcium fluoride is partially decomposed during the fusion step, giving calcium metaphosphate and a volatile fluorine compound. The latter is hydrogen fluoride or silicon fluoride depending on the fusion conditions, contact with silicon dioxide, and other factors. In either event the volatile fluorine can be separated as a useful water treating product. Alternatively the gas mixture from the fusion step can be returned to the carbonation step. The insoluble calcium fluoride leaves the process with the calcium carbonate. In summary regarding fluorine, the fluorine compound can be removed from the fusion gas stream as a useful product or the gas stream can be returned to the carbonation step. Fluorine not attacked by the fusion passes off with the calcium carbonate. Fate of the fluorine depends on economic rather than technical factors.

Iron and aluminum are solubilized during the fusion step. They leave partially via the water wash in step 2 and are returned therewith to the fusion step. After building up in the system they pass to the carbonation step. By the carbonation step the iron and aluminum metaphosphates are at least partially converted to iron and aluminum hydroxides or hydrated oxides. Since in the latter forms and in the phosphates these two metals are insoluble, they are discharged with the calcium carbonate.

The calcium carbonate, calcium sulfate and magnesium oxide impurities apparently are converted to their metaphosphates and then their carbonates in the fusion and carbonation steps respectively.

Thus the impurities are accounted for without undue cost. This is in great contrast to the conventional wet or acid process wherein all the impurities (e. g. $CaCO_3$, CaF_2, $FePO_4$, $AlPO_4$, and $MgCO_3$) consume sulfuric acid and some of them tend to confer poor physical conditions on the resulting product. This is a serious limitation on the grade of phosphate rock that can be employed for sulfuric acid processing. On the contrary low grade rock can be used in the present invention without substantial difficulty.

Another important aspect of this invention is that it is better suited to the recovery of the uranium from phosphate rock during the process of making fertilizer from the rock. During the fusion step the uranium in the rock is converted to uranyl metaphosphate and is carried over in solution in the filtrate from the wash step 2. The uranyl metaphosphate can be separated from this filtrate and the remainder of the water wash recycled to the fusion step. For instance the uranium can be recovered from the water wash by hydration of the metaphosphate (heating the water wash in acid solution) and increasing

an indication of the extent to which this sudden temperature drop was due to endothermic reaction, one fusion experiment was made as described above at an oven temperature of 550° C. along with a blank fusion experiment in which sodium chloride was substituted for the monoammonium phosphate. The results are shown graphically in Figure 6 and the indication is that this temperature drop is due primarily to the chilling effect described above. However, it will be appreciated that this is not an exact blank because the sodium chloride is in a solid state throughout the experiment, whereas the monoammonium phosphate is in a molten state during most of the experiment, and because the heat capacities of sodium chloride and monoammonium phosphate are somewhat different under the conditions of the experiment.

With respect to fusing the monoammonium phosphate alone before mixing and fusing it with phosphate rock and for preparing a water solution of the fused monoammonium phosphate for digestion of phosphate rock, as disclosed hereinbefore, good results were obtained by fusing at a furnace temperature of 350° C.–450° C. for 45–15 minutes, respectively. Fusing at 375° C. furnace temperature for 30 minutes gave particularly good results.

The orthophosphatic material then is removed from the fusion melt (step 2) and returned to the fusion step in order to avoid the problem of reversion during the carbonation step 3. Water may be used to remove the orthophosphatic material, in which case the melt is quenched and/or slurried with water and filtered, the filtrate being evaporated and the residue therefrom recycled to the fusion step. This water treatment also removes any unreacted material from the melt. All that is necessary here is to separate the solid phase from the liquid. True filtration in the usual sense of filtering out a finely divided material is not necessary. Simple decantation or other means of separation suffices.

Next (step 3) the filter cake (which is mostly calcium metaphosphate) from step 2 is reacted with aqueous ammonium carbonate solution, converting the calcium to insoluble calcium carbonate and leaving ammonium metaphosphate in solution. The solution also contains excess ammonia and carbon dioxide. Desirably this conversion reaction is carried out with the calcium metaphosphate in a relatively fine state of sub-division so that there is provided a greater contact area which lessens the reaction time and increases the efficiency of the conversion. Grinding the calcium metaphosphate in admixture with the ammonium carbonate solution until the reaction is substantially complete gives very good results. The ammonium carbonate solution may be introduced as such into the system or, as shown, it may be supplied in the form of ammonia, carbon dioxide and water separately. The use of ammonium bicarbonate along with ammonium hydroxide and water is, of course, equilavent to the use of an aqueous solution of ammonium carbonate as such.

Although the amount of ammonium carbonate used is not critical, it obviously influences the yields of P_2O_5. This may be considered on the basis of the amount of carbon dioxide required to precipitate the calcium as calcium carbonate. The following will give a general picture of the influence of quantity of ammonium carbonate on yields. For example, by employing two times, five times and six times the amount of ammonium carbonate over the theoretical amount required, P_2O_5 yields of approximately 70%, 85% and 90% respectively were obtained.

The concentration of ammonium carbonate employed is important but not critical. As the concentration of ammonium carbonate decreases, the yield of P_2O_5 increases, but the concentration of P_2O_5 in the solution decreases. As the concentration of ammonium carbonate increases, the concentration of P_2O_5 in the solution increases, but the P_2O_5 yield decreases. In the former case very high yields can be obtained but at the expense of much water to be evaporated, whereas in the latter case high concentrations of P_2O_5 prevail at the sacrifice of the exceptionally high yield in the former case. Thus, in order to select optimum conditions, P_2O_5 yields must be weighed against quantity of water to be evaporated.

The calcium carbonate precipitate is filtered off (step 4) as by-product. The filtrate can be processed for taking off as product and for recycling as desired. One means of processing this filtrate to product is by simple evaporation. During this evaporation of this filtrate, a mixture of ammonia, carbon dioxide, and water vapors are evolved. These vapors are condensed to give an aqueous solution of ammonium carbonate which is recycled to the carbonation step 3. If it is desired to employ ammonium metaphosphate for fusing with the rock, then the recycle portion of the monoammonium phosphate can be dehydrated to ammonium metaphosphate before recycling to the fusion step. Alternatively, the filtrate from step 4 can be evaporated to a low volume and the monoammonium phosphate crystallized therefrom by simple conventional means well known to those skilled in the fertilizer art, no particular crystal size and shape being necessary.

The monoammonium phosphate thus produced is exceptionally pure. It shows an analysis 12.2% nitrogen and 61.0% P_2O_5 which are practically the theoretical percentages for monoammonium phosphate. Spectrographic analysis of this product showed only 0.092% iron, 0.0015% aluminum and 0.86% calcium as impurities. The product is a lumpy microcrystalline material which can be crushed very readily to any desired particle size. It takes up substantially no moisture at ordinary ambient atmospheric humidities. A sample of the product was left exposed in the laboratory for several days during a period of very high humidity. Even during this period of exceptionally high humidity the product showed no abnormal or adverse physical conditions.

The importance of the excellent physical conditions and the acceptable physical form cannot be overemphasized. The fact that such a product can be produced by simple evaporation to dryness eliminates the necessity of very careful control, e. g. such as required in a crystallization operation for making a product of a particular crystal size and shape. In the processes for the manufacture of ammonium sulfate, both from gypsum and from the neutralization of sulfuric acid, production of the proper crystal size and shape is quite a difficult problem. While ammonium sulfate of the desired crystal size and shape can be made, it requires very pure solutions as well as careful control of rates of nucleation and growth of crystals in the solution. This means that operators must keep a careful watch on the course of the reaction, thus limiting the capacity of any given plant.

Hereinbefore it is stated that according to this invention either monoammonium phosphate, diammonium phosphate, ammonium metaphosphate or any combination thereof can be manufactured. If diammonium phosphate is desired, a portion of the filtrate is subjected to conditions favorable to hydration of the ammonium metaphosphate to monoammonium phosphate. The resulting solution of monoammonium phosphate is then appropriately ammoniated and evaporated to crystallize out diammonium phosphate. If all ammonium metaphosphate is desired, the filtrate is evaporated under suitable conditions such that hydration of the ammonium metaphosphate to monoammonium phosphate does not take place. Low temperature and high pH favor the recovery of ammonium metaphosphate from this filtrate. For instance this carbonate filtrate was evaporated under the following conditions and very little of the ammonium metaphosphate was hydrated to monoammonium phosphate. The evaporation was carried out at atmospheric pressure; the maxi-

the pH to about 1.5–4, thereby converting the soluble uranyl metaphosphate to insoluble uranyl ammonium phosphate. The uranyl ammonium phosphate precipitates practically quantitatively and is filtered out. This latter filtrate then is recycled to the fusion step.

From the standpoint of uranium recovery the present invention has a number of advantages compared with the wet process. Low grade phosphate rock (low P_2O_5 content) may contain a high uranium content. Low grade rock is not suitable for the wet process, whereas it is for the present invention. The wet process for the manufacture of normal superphosphate is inherently unsuited for the recovery of uranium, yet normal superphosphate accounts for about 90% of the superphosphate manufactured.

This invention, particularly with reference to its preferred embodiment described hereinbefore, is characterized by a number of advantages. The purity and physical properties of the product are remarkably good. The process avoids the inherent difficulties of controlled crystallization by making it possible to separate out such a product by a simple evaporation step. The process does not depend on sulfuric acid or nitric acid or sulfur in any form. The process is comparatively simple and economical. The energy requirements are much less than for conventional fusion processes such as for example the electric furnace process.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

What is claimed is:

1. Process of prepearing soluble phosphatic materials, which comprises fusing calcium-phosphorus containing material and a portion of said soluble phosphatic materials produced by said process, removing orthophosphatic material from the resulting melt, reacting the melt with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the soluble phosphatic materials thus produced as product and recycling a portion of said product to the fusion step.

2. Process of preparing soluble phosphatic materials, which comprises fusing a mixture including primarily phosphate rock and a portion of said soluble phosphatic materials produced by said process, removing orthophosphatic material from the resulting melt, reacting the melt with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the soluble phosphatic materials thus produced as product and recycling a portion of said product to the fusion step.

3. Process of preparing soluble phosphatic materials, which comprises fusing a portion of said soluble phosphatic materials produced by said process, mixing said fused phosphatic materials with phosphate rock, fusing the resulting mixture, removing orthophosphatic material from the resulting melt, reacting the melt with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the soluble phosphatic materials thus produced as product and recycling a portion of said product to the fusion step.

4. Process of preparing soluble phosphatic materials, which comprises fusing a mixture including phosphate rock and a portion of said soluble phosphatic materials produced by said process, washing the resulting melt with water and recycling the washings to the fusion step, reacting the melt, after cooling, with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the soluble phosphatic materials thus produced as product and recycling a portion of said product to the fusion step.

5. Process of preparing soluble phosphatic materials, which comprises fusing a mixture including phosphate rock and a portion of said soluble phosphatic materials produced by said process, washing the resulting melt with water and recycling the washings to the fusion step, reacting the melt, after cooling, with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate substantially to dryness to separate out the soluble phosphatic materials thus produced as product and recycling the evolved gases to the carbonation step, and recycling a portion of said product to the fusion step.

6. Process of preparing soluble phosphatic materials, which comprises fusing phosphate rock and a portion of said soluble phosphatic materials produced by said process, removing the orthophosphatic materials from the resulting melt and recycling same to the fusion step, reacting the melt, after cooling, with an excess of aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate substantially to dryness to separate out the soluble phosphatic materials thus produced as product and recycling the evolved ammonia, carbon dioxide and water vapors to the carbonation step, and recycling a portion of said product to the fusion step.

7. Process of preparing monoammonium phosphate, which comprises fusing calcium-phosphorus containing material and a portion of said monoammonium phosphate produced by said process, removing orthophosphatic material from the resulting melt, reacting the melt with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the monoammonium phosphate thus produced as product and recycling a portion of said product to the fusion step.

8. Process of preparing ammonium metaphosphate, which comprises fusing calcium-phosphorus containing material and a portion of said ammonium metaphosphate produced by said process, removing orthophosphatic material from the resulting melt, reacting the melt with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate substantially to dryness to separate out the ammonium metaphosphate thus produced as product and recycling a portion of said product to the fusion step.

9. Process of preparing monoammonium phosphate which comprises fusing a mixture of phosphate rock and an excess of said monoammonium phosphate produced by said process, removing orthophosphatic material from the resulting melt, reacting the melt with an excess of aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the monoammonium phosphate thus produced as product and recycling a portion of said product to the fusion step.

10. Process of preparing monammonium phosphate, which comprises fusing a mixture of phosphate rock and a portion of said monoammonium phosphate produced by said process, the weight ratio of monoammonium phosphate to phosphate rock being about 3/1, washing the resulting melt with water and recycling the washings to the fusion step, reacting the melt, after cooling, with aqueous ammonium carbonate, the amount of ammonium carbonate used being several times as great as that theoretically required to convert the calcium metaphosphate in the melt to monoammonium phosphate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the monoammonium phosphate thus produced as product and recycling a portion of said product to the fusion step.

11. Process of preparing monoammonium phosphate, which comprises fusing phosphate rock and ammonium metaphosphate prepared from a portion of said monoammonium phosphate produced by said process, removing orthophosphatic material from the fusion melt, reacting the melt with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the monoammonium phosphate thus produced as product, converting a portion of said

product to ammonium metaphosphate and then recycling the latter to the fusion step.

12. Process of preparing monoammonium phosphate, which comprises fusing phosphate rock and ammonium metaphosphate prepared from a portion of said ammonium phosphate material produced by said process, removing orthophosphatic material from the fusion melt, reacting the melt with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to a low volume so as to crystallize out monoammonium phosphate as product, further evaporating the filtrate to separate out the remaining ammonium phosphate material and to convert said material to ammonium metaphosphate, and recycling the latter to the fusion step.

13. Process of preparing soluble phosphatic materials and recovering uranium values from phosphate rock, which comprises fusing phosphate rock and a portion of said soluble phosphatic materials produced by said process during which fusion the uranium is converted to uranyl metaphosphate, washing the resulting melt with water, separating the uranyl metaphosphate from the water wash, reacting the melt with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the soluble phosphatic materials thus produced as product and recycling a portion of said product to the fusion step.

14. Process of preparing soluble phosphatic materials and recovering uranium values from phosphate rock, which comprises fusing phosphate rock and a portion of said soluble phosphatic materials produced by said process during which fusion the uranium is converted to uranyl metaphosphate, washing the resulting melt with water, separating uranyl metaphosphate from the water wash, recycling the washings to the fusion step, reacting the melt, after cooling, with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the soluble phosphatic materials thus produced as product and recycling a portion of said product to the fusion step.

15. Process of preparing monoammonium phosphate

and recovering uranium values from phosphate rock, which comprises fusing about one part phosphate rock and about three parts of said monoammonium phosphate produced by said process during which fusion the uranium is converted to uranyl metaphosphate, washing the resulting melt with water, separating the uranyl metaphosphate from the water wash, recycling the washings to the fusion step, reacting the melt, after cooling, with an excess of aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out the monoammonium phosphate thus produced as product and recycling a portion of said product to the fusion step.

16. Process of preparing monoammonium phosphate, which comprises fusing phosphate rock and a portion of the monoammonium phosphate produced by said process, washing the resulting melt with water, evaporating the washings to crystallize out monoammonium phosphate as product, reacting the melt with aqueous ammonium carbonate, filtering out the calcium carbonate produced, evaporating the filtrate to separate out monoammonium phosphate and recycling same to the fusion step.

References Cited in the file of this patent

UNITED STATES PATENTS

1,074,779	Dunham	Oct. 7, 1913
1,851,210	Palazzo et al.	Mar. 29, 1932
2,086,912	Kaselitz	July 13, 1937

FOREIGN PATENTS

2,724	Great Britain	1863
512	Great Britain	1865

OTHER REFERENCES

Ind. and Eng. Chemistry, Fertilizer by Fusion of Rock Phosphate, vol. 35, No. 7, July 1943.

Ind. and Eng. Chemistry, Calcium Metaphosphate, vol. 36, No. 9, September 1944, pp. 835–840.